

THE STUDY OF HYDROCARBON SURFACE PROCESSES BY THE MULTIPULSE POTENTIODYNAMIC (MPP) METHOD

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INTRODUCTION

The ultimate goal of the hydrocarbon fuel anode researcher is to provide an intellectual basis for the enhancement of system reactivity. As a step toward that goal, we have undertaken the elucidation of the detailed mechanism of operation of a single well-defined system. The ethane-platinum system was chosen for its relative simplicity.

Other than mass transport, the significant reactions of ethane all occur on the platinum surface. Some of the reactions (such as electron transfer) will depend on the electric field strength and may be classed as electrochemical, others (e.g., possible cracking reactions) might be classed as surface-chemical, but in a general sense all are surface processes. It is immediately apparent therefore, that for mechanistic studies of organic electro-oxidation to have any basic significance, such studies must include characterization of the adsorption layer, preferably under anode operating conditions. Such studies come readily within the scope of electrochemical pulse techniques (1,2).

Since we are dealing with a complex adsorbate (ethane) and the platinum surface, we are actually dealing with not one, but a family of systems. Hence it is necessary to investigate a large number of C_1 and C_2 adsorbates (since these will yield pertinent surface species) as well as the adsorption of hydrogen, oxygen and anions. In this paper, we will stress the relationship of two sub-systems (ethylene and acetylene-platinum) to the ethane anode problem.

EXPERIMENTAL

Equipment and Chemicals

The electronic equipment, glass test vessel and electrodes have been described previously (3). The electrolytes used were 1 N perchloric acid and 85% phosphoric acid, each prepared from A.R. grade acid using triply-distilled water. The ethylene and acetylene used was Phillips Research Grade. Gas mixtures of ethylene or acetylene with argon were prepared from the Research Grade hydrocarbon, bottled and analyzed by the Matheson Co. The test electrode was a length of C.P. grade platinum wire sealed in a soft glass tube with 0.070 cm^2 of area exposed. The exposed end of the wire was sealed in a small bead of soft glass. The value of "saturation hydrogen coverage", θ_H , measured as previously (3) was $0.296 \text{ mcoul./cm}^2$, suggesting a "roughness factor" (R.F.) of 1.4 if 0.21 mcoul./cm^2 is taken to correspond to $\text{R.F.} = 1$. All measurements were made in a thermostatted air bath with control to $\pm 0.1^\circ\text{C}$.

Procedure

The potential functions employed are diagrammed in Fig. 1 (time axes not to scale). The procedure followed during each step of Fig. 1 is summarized in Table I along with the significance of the procedure. All potentials were measured against a reversible hydrogen electrode immersed in the adsorbate-free electrolyte.

RESULTS

I. Kinetics of Adsorption of Ethylene and Acetylene

Sequence I, Table I was employed in making these measurements. This sequence is similar to that previously used in the study of CO, (3) in that the passive "oxygen" film is used to hold off adsorption until reduced in step D. The duration of step B and the potential of step C have been decreased to avoid unnecessary exposure to oxidizing conditions (simply as a precaution) without any sacrifice of the surface reproducibility previously reported (3).

The charge corresponding to the oxidation of hydrocarbon adsorbed during step D may be measured by application of sweep E of sequence I, Table I. The traces of Fig. 2a and 2b were obtained at 30°C, using solutions of 1 N perchloric acid saturated with gas mixtures of 1.08% ethylene - 98.92% argon and 0.105% acetylene - 99.895% argon, respectively. The traces of Fig. 3 were obtained at 120°C using an 85% solution of phosphoric acid saturated with a gas mixture of 1.08% ethylene - 98.92% argon. For ethylene, trace 1 of Fig. 2a was obtained in the absence of ethylene, and serves as "solvent correction". The area included between trace 1 and any subsequent trace is a charge Q_{ENE} , which corresponds to the oxidation of the hydrocarbon adsorbed during step D of the sequence. For the sweep speed employed and for the concentration of hydrocarbon used, it may be calculated that the maximum amount of hydrocarbon which may arrive at the electrode (by linear diffusion) and be adsorbed and/or oxidized during step E, is small compared with that already adsorbed during step D. A similar charge, Q_A , may be defined for acetylene from Fig. 2b.

As for ethane (4) it has been found (5) that the charge defined by traces such as those of Fig. 3a and 3b decreases for sweep speeds over approximately 10 v./sec. This is due to retention of a portion of the ad-layer past the duration of the fast l.a.s. The smaller charge measured at higher sweep speeds may be "calibrated" however, so that higher concentrations of adsorbate may be investigated. We may write the expressions:

$$\begin{aligned} 1) \quad Q_{ENE}^* &= a Q_{ENE} \\ \text{and} \quad 2) \quad Q_A^* &= b Q_A \end{aligned}$$

where Q_{ENE}^* and Q_A^* are the high-speed values of charge, and a and b are the proportionality constants relating these charges to the 10 v./sec. values. For example, for 1 N perchloric acid at 30°C, a and b were found to have the values 0.79 and 0.64, respectively for a sweep speed of 100 v./sec. (5). Plots of Q_{ENE} and Q_A vs $T_D^{1/2}$ obtained for the conditions of Fig. 2a and 2b appear in Fig. 4. The linear plots suggest diffusion-controlled adsorption. The relationship for semi-infinite linear diffusion is (3):

$$3) Q_{ENE} = 2n F C_{ENE} D_{ENE}^{1/2} \pi^{-1/2} \tau^{1/2}$$

where n = number of electrons to oxidize and desorb one molecule of adsorbed ethylene

D_{ENE} = diffusion coefficient of ethylene

C_{ENE} = bulk concentration of ethylene (mole/cm³)

and Q_{ENE} is expressed in coul./cm². A similar expression may be written for Q_A . For the ethylene data of Fig. 4, we choose

$C_{ENE} = 3.3 \times 10^{-8}$ mole/cm³ based on the solubility (3.04×10^{-6} mole/cm³, Ref. 6) at one atmosphere in 1 M sulfuric acid at 30°C and assuming applicability of Henry's Law

$D_{ENE} = 1.56 \times 10^{-5}$ cm²/sec. (the value for acetylene in water at 20°C, Ref. 7)

$n = 10$ electrons (assuming complete conversion of a surface C₂H₂ species to carbon dioxide and water)

From these values we obtain:

$$4) Q_{ENE} = 0.147 T_D^{1/2} \times 10^{-3} \text{ coul/cm}^2.$$

which exactly agrees with the experimental plot of Fig. 4. Considering the uncertainty in solubility and diffusion coefficient, the perfect agreement must be assumed to be fortuitous. The occurrence of reasonable agreement serves to establish that the adsorption is indeed diffusion controlled (under these conditions) and that the value of n chosen is probably correct to 20%. For the acetylene data of Fig. 5, we assume the same value of D and n as before. The concentration of acetylene is taken to be

$C = 3.68 \times 10^{-8}$ mole/cm³, based on the solubility in water at 30°C, Ref. 8) and assuming applicability of Henry's Law.

From these values, we obtain a theoretical value of:

$$5) Q_A = 0.164 T_D^{1/2} \times 10^{-3} \text{ coul./cm}^2$$

which is in excellent agreement with the slope of 0.160 of the plot of Fig. 4. Again, the perfection of agreement is probably fortuitous, but the general agreement supports the validity of the assumptions made.

One would not expect diffusion to a wire electrode to follow a linear diffusion law for more than a few seconds (9), which makes the linearity of the plots of Fig. 4 suspect. It is possible to check relationship (3) for values of T_D of less than one second, by using more concentrated solutions of the adsorbate and higher sweep speeds. Results (5) obtained in the fractional second range suggest diffusion-control up to approximately 80% of full coverage, followed by apparent activation control. This latter negative deviation oppose positive deviations from linear diffusion to keep the plots of Fig. 4 linear for large values of T_D .

II. Surface Coverage for Ethylene and Acetylene As A Function of Concentration and Potential.

Sequence II of Table II was employed for these measurements. Although the information required is the extent of adsorption during step E at potential U, steps D and F must be introduced to cope with the complication of surface "oxygen" and with irreversibility of adsorption, within regions of the potential range studied. The approach followed to obtain the data of Fig. 5 - 8, is as follows:

A. Maximum Adsorption at $0 < U \leq 0.6$ V.

1) Starting with Zero Surface Coverage -

T_D and T_F of sequence II, Table I were chosen as zero. The value of Q_{ENE} or Q_A was followed as a function of time at each concentration until a plateau value was reached. The adsorption time was then increased ten-fold to check on whether the maximum value had indeed been attained. An adsorption time somewhat larger than that required was then used to measure adsorption over the potential range. For 0.1% acetylene and 1% ethylene an adsorption time of 100 sec. was satisfactory. For 11% ethylene, 10 sec. suffices and for 0.01% ethylene 200 sec. with stirring suffices.

2) Starting with Full Surface Coverage -

At potentials other than approximately 0.2 - 0.4 v., there are processes of oxidation (high potentials) or hydrogenation-desorption (low potentials) competing with the adsorption process. Attainment of an equilibrium value is apparently very slow. It is possible that equilibrium surface coverage does not exist in the strict sense because of irreversibility in the adsorption, desorption and oxidation processes, further complicated by gradual changes in the structure of the ad-layer. Instead of awaiting apparent equilibrium, we may assume a "quasi-equilibrium" value to correspond to the average of the values achieved when the potential is applied alternatively, to the initially uncovered and fully-covered surface. The latter measurement is accomplished by choosing T_D at the value which results in full coverage for that concentration at 0.4 v. Potential U was applied for a similar length of time T_E , and the resulting decreased values of Q_{ENE} and Q_A were measured.

B. Maximum Adsorption at $U \geq 0.7$ v.

1) Starting with Low Surface Coverage -

At potentials above 0.7 v., the rate of reduction of the passive oxygen film introduced during step B is small (or zero), retarding adsorption. To compensate for this difficulty, T_D was chosen at 1 sec., during which time some (but not complete) adsorption of the hydrocarbon occurred. T_F was also set at 10 msec., to reduce surface "oxygen" deposited during step E, so that this would not interfere with subsequent determination of the surface coverage during the l.a.s.

2) Starting with Full Surface Coverage -

T_D was chosen at the value found to give full surface coverage at 0.4 v. This time also sufficed for complete reduction

of the oxygen film from step B. Step F was chosen at 10 msec. to prevent "oxygen" from interfering with the subsequent measurement of surface coverage.

III. Adsorption (l.a.s.) Traces for CO and Ethane.

Linear anodic sweep traces corresponding to CO surface coverage during adsorption and during oxidation of CO appear in Fig. 9a and 9b respectively. The characteristics of the electrodes used and the method of measurement were described previously (3,10). The sweep speed used was 360 v./sec. Fig. 9a corresponds to adsorption from 1 N perchloric acid saturated with a gas mixture of 1% CO - 99% argon. Fig. 9b corresponds to oxidation at 1.0 v. of a monolayer of CO adsorbed at 0.4 v. from the dilute CO solution. The temperature was 30°C in both cases.

Traces obtained during the adsorption of ethane from a 1 N perchloric acid solution saturated with pure ethane at 30°C, appear in Fig. 10. The conditions under which these traces were obtained were described previously (4).

The conditions under which the traces of Fig. 9 and 10 were measured are similar to those for ethylene and acetylene in that currents corresponding to organic oxidation, correspond only to material on the surface before application of the l.a.s.

DISCUSSION

I. Structure of Adsorbed Ethylene and Acetylene.

We will attempt to deduce certain aspects of the structure of the ad-layer on the basis of the results of measurement of the rate of adsorption, of the shape of the charge (surface coverage) potential plots and of the qualitative appearance of the adsorption (l.a.s.) traces.

A. Terminology Used In Describing the Adsorption Layer.

As there appears to be no generally accepted vocabulary for discussing the details of the ad-layer, the following terms and definitions have been adopted:

Stoichiometry of the ad-layer - The relative amounts of the various elements (carbon, hydrogen, oxygen, etc.) of the adsorbate present on the surface. This is not necessarily the same as the stoichiometry of any single surface species.

Stoichiometry of an ad-species - The relative amounts of the elements present in any particular ad-species. This does not reveal the actual number of atoms of each element in each species.

Composition of an ad-species - The number of atoms of each element present in the ad-species, other than those of the adsorbent. This may be represented as a chemical formula.

Structure of an ad-species - This includes its composition and the nature of the valences between each atom of the ad-species and the nature of each valence between the ad-species and the surface. The "gross" structure permits us to draw a qualitative

diagram showing the bond orientation of the atoms of the ad-species to each other and to the surface. For a heterogeneous surface, we must expect that for each "gross" structure, there will be a number (or perhaps a continuum) of "fine" structures. The fine structure includes information on bond length, bond strength, etc.

Structure of the ad-layer - This includes all information on the structure of the individual ad-species, and on the structure of the adsorbent surface.

As an example of the application of the above terminology, we may describe the structure of the CO ad-layer on Pt, suggested by Eischens and Plisken (11). The stoichiometry of the ad-layer, and the stoichiometry and composition of each ad-species corresponds to the formula CO. It has been suggested that the structure of one CO ad-species (linear) involves a bond from carbon to oxygen and a bond from carbon to one surface site. The structure for a second ad-species (bridged) involves a bond from carbon to oxygen and from carbon to two surface sites. This represents only gross structure since the variations in bond length and strength on various sites of the heterogeneous surface have not been taken into account. The gross structure of the ad-layer includes a certain proportion of the bridged and linear surface species.

B. Adsorption (l.a.s.) Traces for CO.

Results obtained for CO are helpful in demonstrating the effect of changing surface coverage on the characteristics of the adsorption trace of a relatively simple adsorbate. From Fig. 9a, we see that as the surface coverage (charge) with CO increases during adsorption, the shape of the trace changes and there is a marked shift of initial oxidation to the right on the potential axis. Such a shift could occur for a variety of reasons. For CO, it has been suggested that this is because the reaction mechanism involves surface sites not occupied with CO ("reactant-pair" mechanism, ref. 12). According to this explanation, the shift is not caused by a change in gross structure of the ad-species. The important point to be made here is that any attempt to identify an unknown surface species as CO on the basis of the adsorption trace, would be misleading unless comparison were made at (approximately) equal surface coverages. Since the adsorption trace is a highly complex representation of the electrochemical reactivity, it is important that all other conditions (sweep speed, temp., surface preparation) also be held constant. These principles will be used in attempting to arrive at the structure of the hydrocarbon surface species, below.

In the traces of Fig. 9b, the surface is initially covered with a monolayer of CO, and the coverage is progressively decreased by oxidation at 1.0 v. We see that the traces tend to shift back to the left on the potential axis, and when comparison is made at equal values of the surface-coverage, these traces are almost identical with the traces obtained during adsorption (Fig. 9a). Small variations may be due to corresponding variations in the fine structure of the ad-layer. This serves as fair evidence that the gross structure and in particular, the composition of the ad-species does not change at high potentials for this simple adsorbate.

C. Adsorption Traces at $0.2 \text{ v.} < U \leq 0.4 \text{ v.}$ for Ethylene and Acetylene in Perchloric Acid (30°C).

Fig. 2a presents l.a.s. traces ($v = 10 \text{ v./sec.}$) obtained during adsorption at $U = 0.4 \text{ v.}$, of ethylene from perchloric acid at 30°C . We see that a single broad wave was obtained, which shifts to the right on the potential axis with increasing surface coverage (charge). The shift is not as marked as for CO (see Fig. 9). Adsorption at the concentration of adsorbate used in Fig. 2a was complete within 25 sec. The trace for full coverage remained identical for up to 1000 sec., establishing constancy of the structure of the ad-layer over this period of time and at a potential of 0.4 v. Similar traces were obtained for this concentration at a sweep speed of $v = 100 \text{ v./sec.}$ These traces were then compared with those obtained using a ten-fold more concentrated solution for which full coverage is achieved within approximately 500 msec. The traces for identical surface coverage but different adsorption times could be exactly superimposed. On the basis of these experiments one may conclude that over the entire range of surface coverages the structure of the ad-layer remains constant from the fractional-second to the 1000 second range. Comparison of traces obtained at 10 v./sec. for $U = 0.2, 0.3$ and 0.4 v. reveal that the same statement may be made for each of these three potentials.

Traces for adsorbed acetylene appear in Fig. 2B. The dashed traces allow comparison of each trace with that of ethylene at a value of $Q_{\text{ENE}} = Q_A$ (to within 10%). We see that the comparable traces are almost identical. We tentatively conclude that the structure of the ad-species is the same for both adsorbates. The slight difference in the traces is ascribed to differences in fine structure of the ad-layer (perhaps a different distribution of species on the surface). Study of the traces reveals constant structure of the ad-layer over the same time and potential interval as for ethylene.

D. Adsorption Traces for Ethylene and Acetylene at $U \geq 0.5 \text{ v.}$ in Perchloric Acid (30°C).

Fig. 5a and 5b present l.a.s. traces for ethylene and acetylene respectively for values of U from 0.3 to 0.8 v. Traces 2 and 3 of each figure are included to emphasize that the adsorption of less material at 0.3 v. is reflected in a shift of the trace to the left on the potential axis. Traces 4 and 5 of each figure represent lower values of surface coverage (charge) than trace 3, but these traces lie to the right of trace 3. This shift to the right is clear indication that the structure of the ad-layer is different at the higher potentials. This change is first (barely) discernible at 0.5 v. One could argue that this represents only differences in the fine structure of the ad-layer. For example, the composition of the ad-layer might be the same as at lower potentials, but only sites involving relative inactivity (toward electrochemical oxidation) of the ad-layer might be covered. For CO, we have seen that there is no such marked change in reactivity of the ad-layer as we approach a given surface coverage alternatively from zero coverage at low potential, or from full coverage at high potential. By analogy, we conclude that the marked shifts in the traces of Fig. 3 correspond to gross changes in structure; namely, to changes in the composition of the ad-species. Hydrogen codeposition measurements support this view (5). One possibility is that de-hydrogenation of

the surface species leads to a stoichiometry approaching that of carbon. This choice is made tentatively, based on the observation that all oxygen-containing carbon compounds examined to date show higher reactivity than that suggested by traces 4 and 5 of Fig. 3.

E. Inferences from the Results of Measurement of Kinetics of Adsorption of Ethylene and Acetylene.

Thus far, the evidence suggests that identical ad-species are obtained upon adsorbing either ethylene or acetylene at potentials below 0.5 v. The simplest possibility for the stoichiometry of the ad-layer is therefore CH. Excellent agreement with diffusion theory was shown (in a previous section) if we assumed that 10 electrons are required for the oxidation-desorption of one mole of either adsorbate. This is precisely the electron requirement for conversion of the adsorbates to CO₂ and water through surface intermediates of CH stoichiometry. Since the solubility and diffusion coefficients could not be expected to be reliable to more than 20%, somewhat smaller ratios of hydrogen to carbon are also consistent with the kinetic observations. These observations fairly conclusively rule out the presence of any oxygen in the ad-species ($U < 0.5v.$), however, since this would drastically change the value of "n".

The composition of the ad-species obtained at low potential is suggested by results obtained by Niedrach (13). He found that hydrogenation-desorption of an adsorbed ethylene layer yielded predominately ethane, arguing for the conservation of the carbon-carbon bond. Hence at low potentials and temperatures we conclude that the ad-species have the composition C₂H₂. At higher potentials we tentatively conclude the formation of species of composition C₂H and C₂.

F. Structure of Ethylene Adsorbed at Temperatures Above 30°C.

The adsorption traces obtained at 60°C in perchloric acid were similar to those obtained at 30°C, with a slight shift of the traces to the left on the potential axis. As before, only one broad wave was apparent. Measurement of Q_{ENE} after an adsorption time of 8 sec. in a solution saturated with a gas mixture of 1.08% ethylene-98.92% argon, yielded a value 20% higher than the corresponding value at 30°C. This is a reasonable result if we assume diffusion-controlled adsorption (as at the lower temperature) and an increase in the diffusion coefficient of about 40%. Hence we conclude that the structure of the ad-species and the mechanism of adsorption is the same at 60° and 30° in perchloric acid.

For ethylene in phosphoric acid at 120°C, the adsorption traces (Fig. 4) are considerably different than in perchloric acid. Not only does oxidation of the ad-layer begin at lower potentials, but an inflection appears in each trace, suggesting two overlapping waves. This may be symptomatic of the formation of species containing a single carbon atom following rupture of the carbon-carbon bond. The values of Q_{ENE} obtained under these conditions do not have linear dependence on $T^{1/2}$ and the adsorption is therefore relatively slow (compared with diffusion). Whereas the increased reactivity of the ad-layer is readily ascribed to the effect of increased temperature, the explanation for the slow kinetics of adsorption is not obvious. One possibility is that the surface species formed at this higher temperature tend to exert long-range ("poison") effects on the surface.

Another possibility is that adsorbed phosphate ions (14) influence the kinetics of adsorption.

G. Structure of Adsorbed Ethane.

Adsorption traces for ethane at 60°C in perchloric acid appear in Fig. 11. As previously (4) indicated, each trace consists of a peak lying at relatively low potentials and of a broad maximum which extends from about 0.8 v. to oxygen evolution potentials (at $v = 10$ v./sec.). The first peak is largely retained upon application of potentials approaching 0 v. Niedrach (15) has suggested that the first peak corresponds to C - 1 species. The broad maximum is removed by hydrogenation-desorption and it has already been suggested that this species has C_2H_2 composition on the basis of other evidence (4). This work tends to confirm that conclusion for potentials in the range 0.2 - 0.4 v. Since the evidence suggests that the C_2H_2 species convert (possibly further dehydrogenate) at higher potentials, this must also be true for the ethane system.

II. Dependence of Surface Coverage On Concentration, Potential and Temperature for Ethylene and Acetylene.

A. Significance of Q_{ENE} and Q_A .

In perchloric acid, in the potential range 0.2 to 0.4 v., the results suggest that the charges Q_{ENE} and Q_A correspond to the conversion of surface species of the composition C_2H_2 to CO_2 and H_2O . Hence we may write:

$$6) \quad Q_{ENE} = n \Gamma_{ENE} F = 10 \Gamma_{ENE} F$$

where Γ_{ENE} is the concentration of the ad-species in moles/cm², if Q_{ENE} is expressed in coul./cm² (of geometric area). Conversion to a "true area" basis may be made by dividing by the estimated surface R.F. of 1.4. A similar expression may be written for acetylene.

The fractional surface coverage with an adsorbate is commonly defined in terms of the experimental maximum value (although vacant sites may still exist). In terms of charge, we may write:

$$7) \quad \theta_{ENE} = Q_{ENE}/Q_{ENE(max.)}$$

where $Q_{ENE(max.)}$ is the largest plateau value observed on the charge-potential plots. A similar expression may be written for acetylene.

Since we suspect dehydrogenation of the ad-species at potentials above 0.4 v., the value of n of equation (6) may drop from 10 to a minimum of 8. This can introduce an error of no more than 20% in the estimation of either absolute or fractional surface coverage.

"Saturation" surface coverage (perchloric acid, 30°C) for ethylene and acetylene adsorbates corresponds to values of $Q_{ENE} = 0.64 \times 10^{-3}$ coul./cm² and $Q_A = 0.73 \times 10^{-3}$ coul./cm². These charges are equivalent to $\Gamma_{ENE} = 6.6 \times 10^{-10}$ mole/cm² (geometric area) or 4.7×10^{-10} mole/cm² (hydrogen or "true" area) and $\Gamma_A = 7.6 \times 10^{-10}$ mole/cm² (geometric area) or 5.4×10^{-10} mole/cm² ("true" area). From hydrogen codeposition experiments (5) only 75% of the hydrogen sites are obscured by C_2H_2 at full coverage using ethylene as adsorbate,

and 85% of the sites are obscured using acetylene as adsorbate.

B. Effect of Potential on the Surface Coverage for Ethylene and Acetylene.

From Fig. 7, we see that for both ethylene and acetylene, the surface coverage is constant over the potential range 0.2 to 0.4 v. For potentials below 0.2 v., the surface coverage drops off sharply. Burke et al. (16,17) have shown that the hydrogenation of ethylene and acetylene are diffusion controlled, and not quite diffusion controlled, respectively, at 0 v. It is the hydrogenation process, opposing the adsorption process, which causes the surface coverage to drop off at the low potentials. For both acetylene and ethylene, we note that different coverages are measured at a given potential, depending on whether the experiment is begun with zero ($T_p = 0$) or full surface ($T_p = 100$ sec.) coverage. The average value for each of the potentials probably approximates an equilibrium value.

The surface coverages obtained for ethylene and acetylene at potentials below 0.2 v. are noticeably different. This seems an anomaly if one accepts the conclusion that the composition of the ad-species is identical for both adsorbates. An explanation of this behavior is presented below.

Let us assume that adsorption must precede hydrogenation (in the limit, the surface coverage may be almost zero, however). For acetylene, the composition of the ad-species is the same as that of the adsorbate. At potentials below 0.2 v., there will be two competing reactions, i.e., the adsorption of C_2H_2 and the hydrogenation of surface C_2H_2 . Both rates may be expected to be a function of surface coverage and of potential. Starting with either the fully-covered, or uncovered surface, the system will attempt to reach equilibrium at a value of the surface coverage at which the two rates are equal. If the rates in question are complex functions of the surface coverage, and of the concentration of dissolved acetylene, equilibrium may be attained rather slowly, as seems to be the case.

For ethylene at potentials below 0.2 v., we might expect the operation of three kinetic processes, i.e., adsorption of ethylene to yield C_2H_2 surface species, hydrogenation of adsorbed C_2H_2 to yield ethane and (unlike the situation for acetylene adsorption), the hydrogenation of C_2H_4 (present at close to zero concentration on the surface) to yield ethane. Only the second process is held in common with the acetylene adsorbate system, hence one would expect to arrive at different equilibrium coverages for the two systems.

The lower values of surface coverage obtained (below 0.2 v.) for ethylene as compared with acetylene can be a consequence of a slower adsorption step, or of an appreciably larger rate for the reduction of the C_2H_4 species. Since the over-all rate of formation of ethane from ethylene is larger than for acetylene (14,15) the latter condition must be fulfilled. This is also an intuitive conclusion, if we accept the conclusion that the dehydrogenation of C_2H_4 to C_2H_2 on the surface is a spontaneous process throughout the potential range studied.

In the region of the flat plateau for ethylene and acetylene (Fig. 8) we see that the surface coverage for acetylene adsorbate exceeds that for the ethylene adsorbate by approximately 10%.

Hydrogen co-deposition experiments (5) reveal that only approximately 85% of the total (hydrogen) sites are covered even for the acetylene system. Since adsorption of ethylene requires a dehydrogenation on the surface (to C_2H_2) it seems reasonable to conclude that the surface might be sterically blocked at lower values of the surface coverage than for acetylene, for which system no surface dehydrogenation is necessary.

At potentials above 0.4 the surface coverage drops off with increasing potential for both acetylene and ethane. Both of these adsorbates undergo oxidation at these potentials. One might argue that full coverage should yet be attained unless the oxidation process were diffusion-controlled, because only then would it exceed the rate of adsorption. However, the rate of adsorption is only rapid at potentials within the range 0.2 - 0.4 v., where the ad-species are of constant composition. At potentials above 0.4, we have already seen evidence that the ad-species change composition. Results of measurement of rates of re-adsorption (5) suggest that as the potential increases, almost a combined monolayer of the hydrogen-poor species and surface oxygen results, with the latter contribution increasing with potential. The rate of adsorption from the point of incomplete coverage to full coverage is relatively slow. Since the rate of re-adsorption may be expected to depend also on the concentration of the adsorbate, we find the concentration-dependencies of Fig. 6.

C. Effect of Concentration of the Adsorbate On Surface Coverage.

For ethylene, the effect of concentration on Q_{ENE} (and hence on the surface coverage) is presented (perchloric acid at 30°C) in Fig. 6. In the (potential) region of maximum Q_{ENE} , we see that there is no methodical increase in surface coverage with concentration, of the type generally associated with the adsorption isotherms of systems exhibiting thermodynamically reversible adsorption. The maximum surface coverage is taken as essentially constant over the range of partial pressures covered. The average maximum value of Q_{ENE} is 0.62 mcoul./cm², with an average deviation of ± 0.02 mcoul./cm², or $\pm 3\%$ average deviation. The occurrence of full (effectively, since all adsorption sites are not necessarily covered) coverage at low partial pressures of adsorbate is not uncommon for systems which possess a high heat of adsorption.

In the potential range above 0.4 v., we see considerable effect of concentration on the surface coverage. The surface coverage at steady-state (assuming that such a state exists in practice for an ad-layer which may undergo continuous change in structure with time) would correspond to the value at which the rates of adsorption and of oxidation are in balance. Both of these rates may be complex functions of surface coverage, but the rate of adsorption must also be a function of concentration of dissolved adsorbate. Hence it is particularly the rate of adsorption which must decrease with decreasing concentration of adsorbate, and the surface coverage falls. It must be borne in mind, that in the range of potentials above 0.4 v., we are not dealing with diffusion-controlled rates of adsorption, as at lower potentials, since the structure of the ad-layer is more complex. It is probably the high rate of adsorption (relative to oxidation) that maintains a flat maximum over a wide range of potentials for the most concentrated adsorbate of Fig. 6, when the experiment is begun with full coverage. The slow approach toward equilibrium

is further argument against the shape of the surface coverage-potential plot's being determined by essentially electrostatic forces.

D. Effect of Temperature On Surface Coverage.

Fig. 8 reveals that at 60°, the maximum surface coverage achieved for ethylene is 5% higher than at 30°C. In either case, all adsorption sites are not fully occupied. One way in which the temperature may increase "full" coverage is to increase the mobility of the ad-layer, permitting closer packing of the ad-species.

It has already been noted that at 120°C and in phosphoric acid, the kinetics of adsorption and the composition of the ad-layer are complex. Values of Q_{ENE} up to 0.83 mcoul./cm² could be measured (adsorption for 100 sec.). If we assumed C₂H₂ composition of the ad-layer, this would be equivalent to 95% of full coverage (on basis of available hydrogen sites). It is not unlikely that the large value of charge actually corresponds to close packing of considerable C-1 species.

E. Comparison with the Results of Tracer Studies.

The adsorption of ethylene on platinized platinum (1 N sulfuric acid, 30 and 80°C) has been investigated by J.O'M. Bockris et al. (18), using tracer techniques. The results of this work disagree with those of our predecessors in several ways. An attempt to reconcile this disagreement appears below, on the basis that the only significant difference between the two systems is the surface roughness. Bockris (18) observes only a gradual increase of surface coverage with concentration from approximately 10⁻⁶ to 1.5 x 10⁻⁵ mole/l. bulk concentration of ethylene, with full coverage achieved at the higher concentration. In this work we attained full coverage at a concentration of 3 x 10⁻⁷ mole/l. (1.3 x 10⁻⁴ Atmos.). In our experiments, the adsorption was transport-controlled and required approximately 200 sec. for completion in a well-stirred solution (3 x 10⁻⁷ M./l.). By comparison, adsorption from a 10⁻⁶ M./l. solution would require 20 sec. for our system. For a platinized electrode with a R.F. of 100, as used by our predecessors, an equilibration time of 2000 sec., or approximately 30 minutes would be required. It is possible that such time durations were not allowed routinely. A second possibility is that the 100 fold greater rates of oxidation (on basis of geometric area) and hydrogenation-desorption encountered on the platinized electrode, tend to result in partial diffusion control for these reactions even at low potential, forcing the surface coverage down.

Bockris et al. (18), also found that maximum adsorption was attained only at higher potentials than in this work. The decrease in surface coverage encountered in this work, as the potential is lowered to less than 0.2 v., has been ascribed to the effect of the opposing rate of hydrogenation-desorption, which increases as the potential is lowered. For the platinized surface this rate would be increased 100-fold at comparable potentials. Such an enhanced rate might lead to sufficient depletion of the adsorbate to drive the surface coverage down at approximately 0.3 v., as found by Bockris.

III. Mechanism of the Electrochemical Oxidation of Hydrocarbons.

The studies of adsorption reported in this paper are a necessary preliminary to future detailed study of the mechanism and kinetics of the electrochemical oxidation of the hydrocarbons. It is possible at this time, however, to draw some qualitative conclusions on mechanism, based on the available information.

The rate of continuous oxidation of any complex molecule which yields a variety of surface intermediates, may be expressed in terms of the partial currents for each of "n" surface species:

$$8) \quad I_i = n_i F k_i f_i (\theta_1, \theta_2, \dots, \theta_n) g_i(U)$$

where n_i = number of electrons required to convert species "i" to the next identifiable surface species

k_i = appropriate rate constant

f_i = a function relating the current for species "i" to the surface coverage with the various species (assuming interaction)

g_i = a function relating the current to the applied potential for species "i"

Equation (8) also covers the situation for any reaction path requiring an adsorbed intermediate, even if the effective concentration of that species is vanishingly small. In addition there may be "m" reaction paths involving the initial reactant in the non-adsorbed state (Rideal-Eley as opposed to Langmuir-Hinshelwood mechanism, ref. 19):

$$9) \quad I_j = n_j F k_j h_j (\theta_1, \theta_2, \dots, \theta_m) j_j(U)$$

where the symbols have significances similar to those for equation (8). The total current may then be expressed as:

$$I = \sum_{i=1}^n I_i + \sum_{j=1}^m I_j$$

Since ethylene, acetylene and ethane all hold one group of surface species in common, we may discuss the qualitative dependence of the corresponding partial current on surface coverage, bearing in mind that this is a small part of a much larger problem area.

For the potential range 0.2 - 0.4 v. in perchloric acid, it appears that we have the common surface species C_2H_2 . The traces of Fig. 2 reveal that as the surface coverage with this species increases, the corresponding trace shifts to the right on the potential axis, or in other words, the initial oxidation becomes increasingly more hindered. One interpretation is that the electronic character of the surface changes with surface coverage. A more tangible possibility is that the transition state for oxidation of the surface species, involves surface sites not blocked by the hydrocarbon ("free" sites). The similar observation for CO (see Fig. 9) led to the suggestion of a "reactant pair" mechanism, involving adjacent sorbed CO and water molecules (3). For the complicated C_2H_2 structure there are several plausible explanations for similar dependence of oxidation rate upon free sites. These

include the requirement of extra sites for the rupture of carbon-carbon and carbon-hydrogen bonds. Additional information will be required before a conclusion may be reached in this area.

For the potential range above 0.4 v. (perchloric acid), the l.a.s. traces of Fig. 5 reveal that the ad-species formed at higher potentials undergo initial oxidation less readily than does the C_2H_2 surface species. On this basis it has already been suggested that the structure may be approaching C_2 stoichiometry at the high potentials. If this conclusion is correct, sequential dehydrogenation is one of the possible paths for the oxidation of all of the C - 2 hydrocarbons. It is apparently the path of smallest specific rate for ethane, for which a low potential wave appears in the l.a.s. trace (Fig. 10). For ethane, it has been suggested that an adsorbed ethyl radical is the common antecedent of both reaction paths (4). The more reactive path is believed to involve C - 1 species (15).

CONCLUSIONS

1. Under the conditions of our experiments, the adsorption of ethylene and acetylene from perchloric acid was diffusion-controlled. The early onset of diffusion control implies very rapid adsorption kinetics (equivalent to a first order electrochemical rate constant of greater than 0.1 cm/sec.) at low surface coverages.

2. The results of the adsorption measurements suggest that the composition of the ad-species for both ethylene and acetylene adsorbates is identical. In perchloric acid, at potentials of 0.4 v. or less, the ad-species has the composition C_2H_2 . At potentials above 0.4 v., the ad-layer becomes more refractory, possibly because of further de-hydrogenation of the acetylenic surface species. There is no evidence for conversion of the C_2H_2 species to more easily oxidized "oxygenated" species at moderate temperatures.

3. In phosphoric acid at 120°C, the kinetics of adsorption of ethylene follows a complex law. The structure of the ad-layer is also complex. It is possible that both temperature and specific anion effects play a significant role in the system.

4. The adsorption of ethane from perchloric acid is slow, and yields two categories of surface species represented as two "waves" on the linear anodic sweep traces. Wave I is not (significantly) desorbed at low potentials, and is comparatively electrochemically active (with respect to oxidation). Wave II is readily desorbed at low potentials and is identical with the acetylenic species obtained upon adsorbing ethylene or acetylene. At moderate temperatures, wave II does not convert to I at any appreciable rate and hence (in a sense) acts as an undesired residue as compared with wave I. The variation, with potential, of the composition of the ad-species represented by wave II is the same as that reported for ethylene or acetylene.

5. Full coverage of the surface is obtained (in perchloric acid) at partial pressures of ethylene as low as 10^{-4} atmospheres. The shape of the surface-coverage-potential plot for both ethylene and acetylene is consistent with a model such that the surface coverage is driven down at the low and high potential regions by rates of hydrogenation-desorption and of oxidation, which oppose

the rate of adsorption. In the high-potential region, the combined coverage of adsorption sites with multiply-bonded carbon species and with "oxygen" is high, even though the surface concentration of the organic species appears low on a Mole/cm² basis. The rate of adsorption of ethylene or acetylene on a surface partially covered with the high-potential carbon species is very slow compared with that on a surface partially covered with C₂H₂.

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Table 1.-PROCEDURES FOLLOWED DURING POTENTIAL SEQUENCES OF FIG. 1

Sequence	Fig.	Step (refers to Fig. 1)	Procedure	Purpose
I	1(a)	A	1. Potential normally held at 0.4 v. between experiments.	1. To minimize exposure of electrode and adsorbate to oxidizing or reducing conditions.
		B	2. Bubble gas* through solution with paddle-stirring for $T_B = 2$ seconds†.	2. To remove adsorbed materials from the surface, and to produce a passive film which blocks re-adsorption.
		C	3. Continue gas bubbling, and stirring for 1/2 minute. Stop bubbling and stirring and allow solution to become quiescent for 1 1/2 minutes. Total value of $T_C = 2$ min.	3. The passive film of step B is retained while desorbed materials and oxygen released during step B are swept into the bulk of the solution and diluted. The solution is allowed to become quiescent to restrict mass transport to ordinary diffusion in subsequent steps.
		D	4. The adsorption is allowed to proceed for T_D seconds.	4. The passive film is largely reduced during the first few milliseconds, allowing adsorption of the hydrocarbon from solution.
		E	5. Apply linear anodic sweep E of speed, v.	5. The amount of material adsorbed during time interval T_D may be determined from the l.a.s. trace.
II	1(b)	A - D	1 - 4. Same as for Sequence I.	1 - 4. Same as for Sequence I.
		E	5. The potential is raised (or lowered) to value U, for time T_E .	5. Further increase, or decrease occurs in the surface coverage acquired in step D.
		F	6. Apply l.a.s. F, of speed v.	6. The amount of material on the surface may be determined from the l.a.s. trace. This amount will be a function of T_D and T_E .

* The gas used was a designated mixture of argon and hydrocarbon.

† "T" with the appropriate subscript is the duration of any particular step.

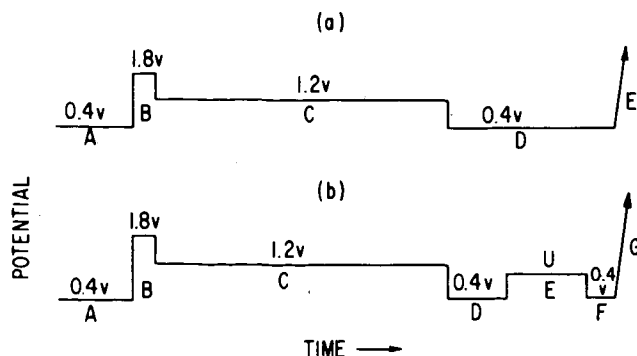


Fig. 1.-POTENTIAL SEQUENCES APPLIED TO THE TEST ELECTRODE (TIME AXES NOT TO SCALE).

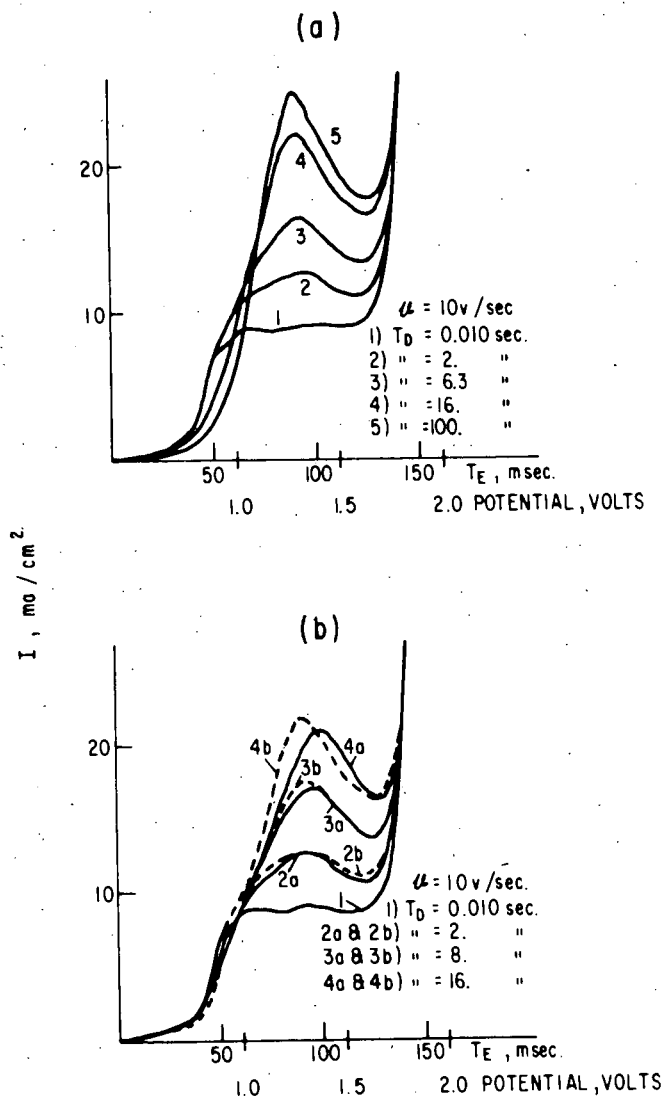


Figure 2. L.A.S. Traces Corresponding to the Adsorption at 0.4 v., of Ethylene and of Acetylene (1 N HClO₄, 30°C). Traces measured using Sequence I, Table I, with $v = 10 \text{ v./sec.}$ The traces of Fig. 2a and the dashed traces of Fig. 2b correspond to 10^{-2} atmospheres of ethylene. The solid traces of Fig. 2b correspond to 10^{-3} atmos. of acetylene.

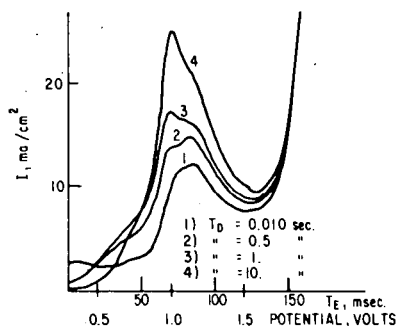


Fig. 3.-L.A.S. TRACES CORRESPOND TO THE ADSORPTION OF ETHYLENE FROM 85% PHOSPHORIC ACID AT 120°C (ETHYLENE p.p. = 10^{-2} ATMOSPHERES). TRACES MEASURED USING SEQUENCE I, TABLE I, WITH $v = 10 \text{ v./sec.}$

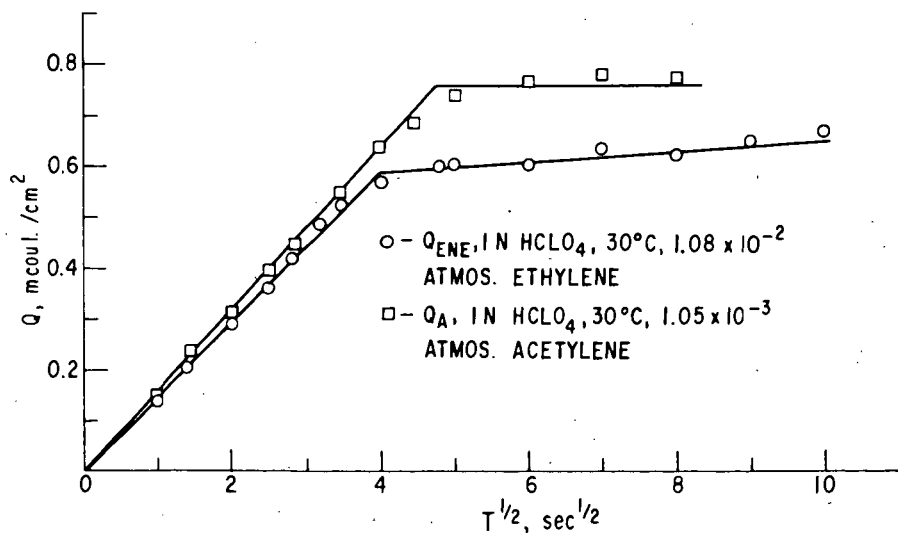


Fig. 4.-KINETICS OF ADSORPTION OF ETHYLENE AND OF ACETYLENE FROM 1 N HClO₄. THE ABSOLUTE SURFACE COVERAGE IS PROPORTIONAL TO THE CHARGE, Q (SEE TEXT).

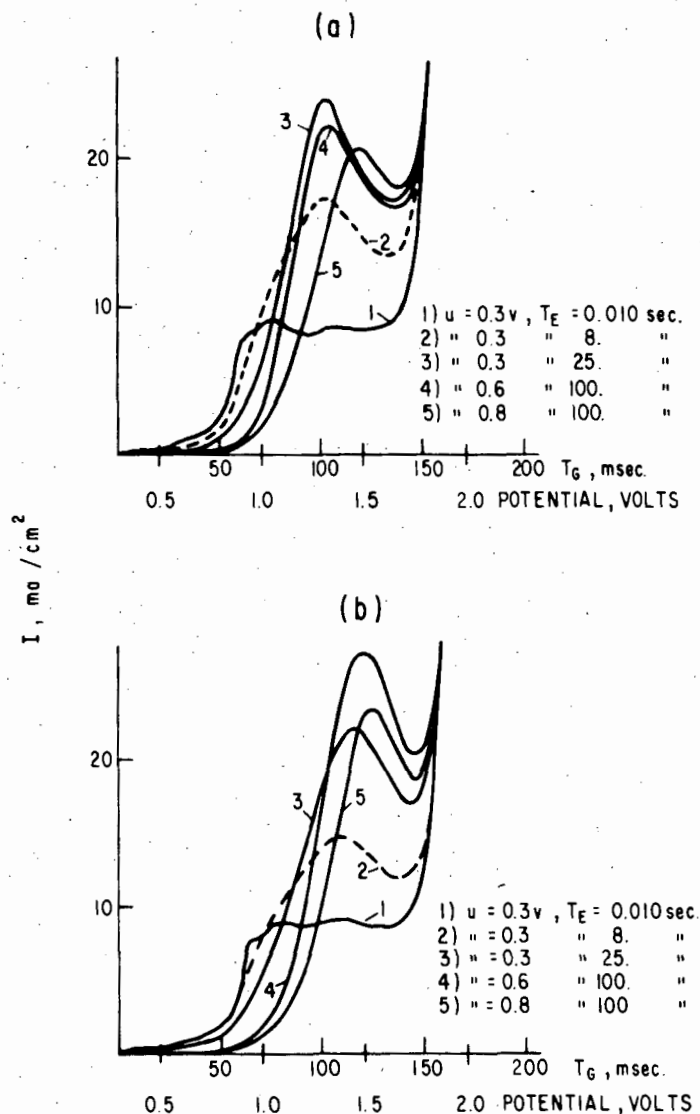


Figure 5. L.A.S. Traces Corresponding to the Adsorption of Ethylene and of Acetylene at Various Potentials (1 N HClO_4 , 30°C.). (a) p.p. of ethylene = 10^{-2} atmospheres, (b) p.p. of acetylene = 10^{-3} atmospheres. Traces measured using Sequence II, Table I, with $v = 10 \text{ v./sec.}$

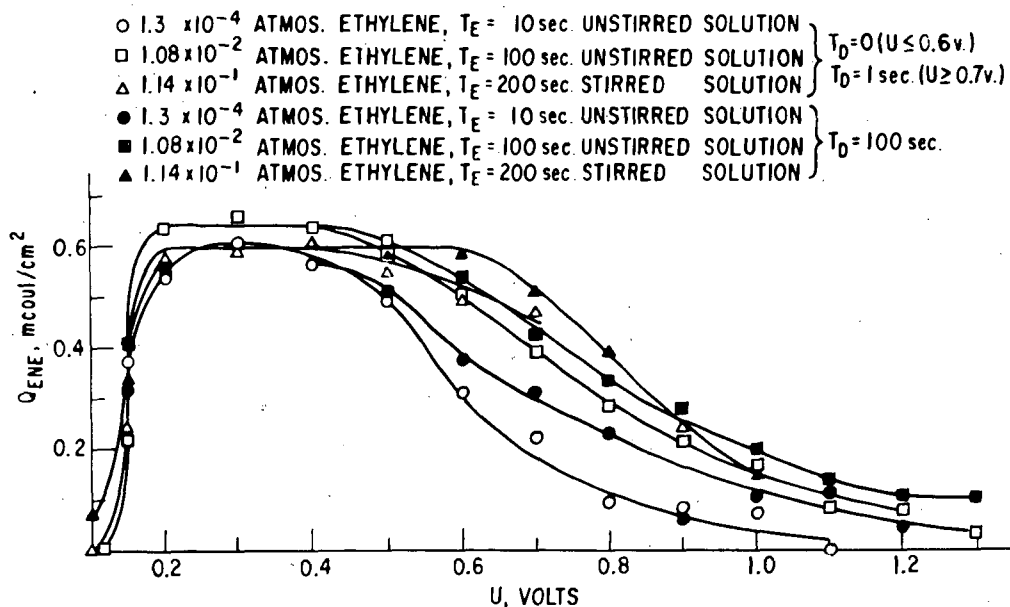


Fig. 6.-VARIATION OF SURFACE COVERAGE WITH ADSORBATE PARTIAL PRESSURE AND WITH POTENTIAL, FOR ETHYLENE (1 N HClO₄, 30°C). FRACTIONAL SURFACE COVERAGE MAY BE DERIVED BY NORMALIZING THE MAXIMUM CHARGE TO 1.

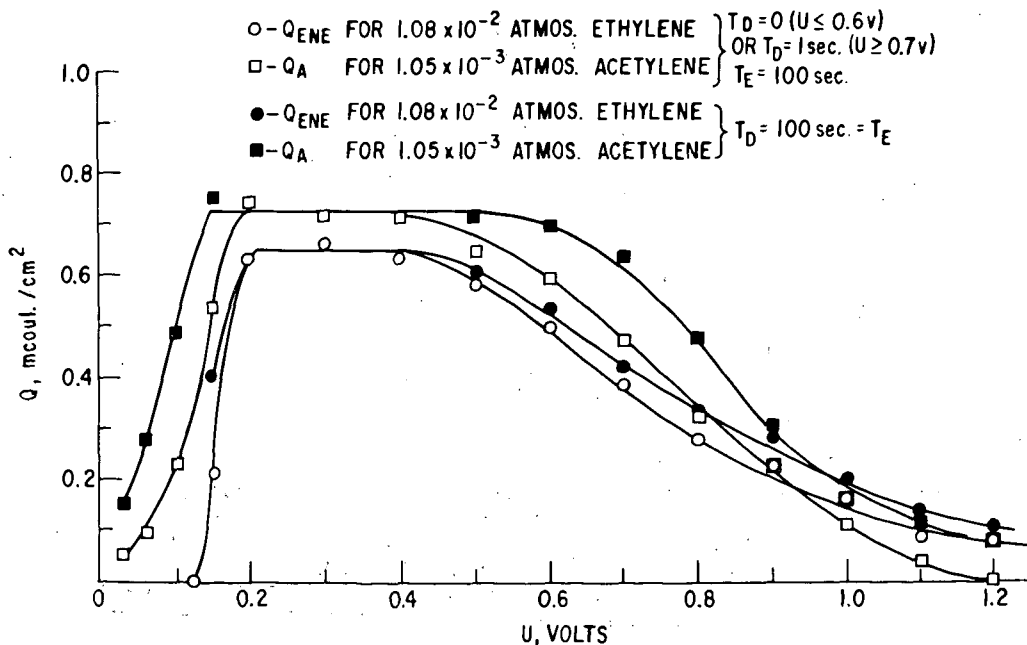


Fig. 7.-VARIATION OF SURFACE COVERAGE WITH POTENTIAL FOR ETHYLENE AND FOR ACETYLENE (1 N HClO₄, 30°C, ETHYLENE p. p. = 10^{-2} ATMOSPHERES, ACETYLENE p. p. = 10^{-3} ATMOSPHERES).

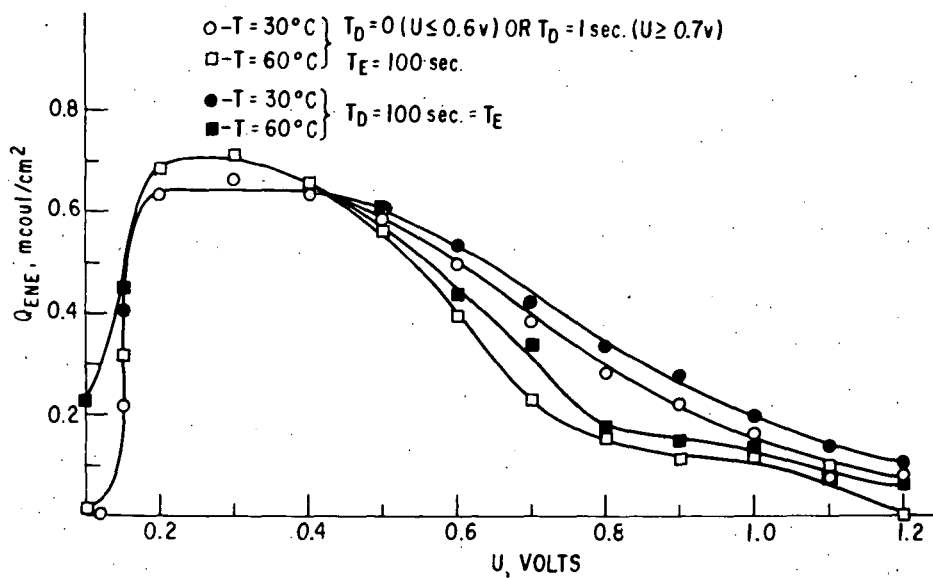


Fig. 8.-VARIATION OF SURFACE COVERAGE WITH POTENTIAL AND TEMPERATURE FOR ETHYLENE AND FOR ACETYLENE.

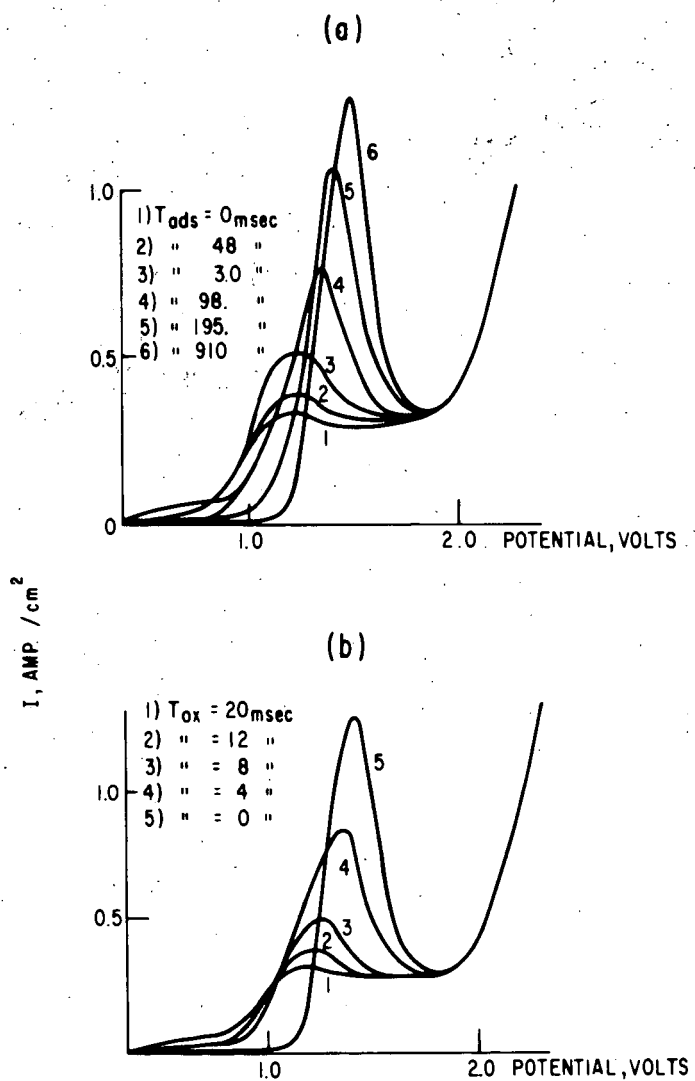


Figure 9. L.A.S. Traces for Adsorbed CO (1 N HClO_4 , 30°C , CO p.p. = 10^{-2} atmospheres, $v = 360 \text{ v./sec.}$). (a) corresponds to the adsorption for time, T_{ads} ; (b) corresponds to the oxidation for time T_{ox} , of a monolayer of CO.

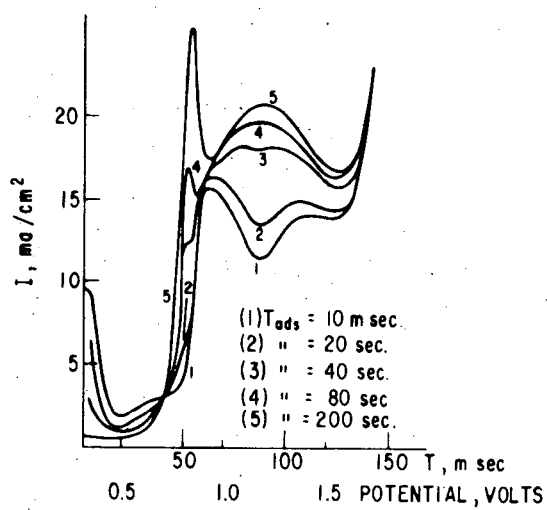


Figure 10. L.A.S. Traces Corresponding to the Adsorption of Ethane for Time, T_{ads} . (1 M HClO_4 , 60°C , p.p. ethane = 1 atmosphere, $v = 10$ v./sec.).